Title: **Water-gas Shift with Integrated Hydrogen Separation Process**

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Abstract

Advanced catalysts for the water-gas shift (WGS) reaction are actively being sought for use in fuel cell power generation for both stationary and transportation applications. Optimization of the WGS system for hydrogen production for fuel cells is of particular interest to the energy industry. To this end, it is desirable to couple the WGS reaction to hydrogen separation using a semi-permeable membrane, with both processes carried out at high temperature and pressure to improve reaction kinetics. Reduced equilibrium conversion of the WGS reaction at high temperatures is overcome by product H_2 removal via the membrane.

This project involves fundamental research and development of novel cerium oxide-based catalysts for the water-gas-shift reaction and the integration of these catalysts with thin Pd-alloy, H_2-separation membranes supplying high purity hydrogen for fuel cell power generation. Conditions matching the requirements of coal gasifier-exit gas streams are examined in the project. The approach taken in this work is to treat the WGS catalyst and membrane as a single, tightly coupled system designed to operate efficiently over a wide temperature window. This is possible when a hydrogen-selective membrane of high permeance is juxtaposed to a highly active catalyst that, accordingly, maintains a substantial driving force for H_2 permeation.

In screening studies of WGS catalysts we identified Cu-ceria as the most promising high-temperature shift catalyst for integration with H_2-selective membranes. Formulations containing iron oxide were found to deactivate in CO_2- rich gases, and were thus eliminated from further consideration. Cu-containing ceria catalysts, on the other hand, showed high stability in CO_2-rich gases. This type gas will be present over much of the catalyst, as the membrane removes the hydrogen produced from the shift reaction. Catalyst formulations particularly active in WGS involve La-doped ceria. A dopant level of 30 at% was found to give peak activity. Experiments with 10at%Cu-Ce(30at%La)O_x were conducted over the temperature range 300- 450^{o}C in simulated coal gases and in CO_2-rich gas streams. Detailed evaluation of this type catalyst including reaction kinetics after aging in the reaction mixture took place this past year. WGS

reaction rates were measured over the 10%Cu-Ce(30%La)O_x and the copper-free Ce(30%La)O_x catalysts in the simulated coal-gas mixture 11%CO-23%H_2O-11%CO_2-17%H_2-He. The activation energy of the reaction over these catalysts is 70 kJ/mol and 98 kJ/mol, respectively. This large difference is due to the modification of the surface of ceria by the addition of copper. As discussed in last year's report, addition of copper greatly increases the reducibility of the surface oxygen of ceria. The reaction pathway on copper-free ceria is different, and of larger activation energy. At high temperatures, such as 450^o, fresh 10%Cu-Ce(30%La)O_x loses about 30% of its initial activity in a few hours. To obtain a stable conversion and reaction rate, and an accurate measurement of the activation energy, we measured the reaction rate over the 10%Cu-Ce(30%La)O_x sample after it had been used in the reaction gas mixture at 450^{o}C for 20 h. The reaction orders in CO, H_2O, H_2, and CO_2 are 0.8, 0.1, -0.3, and –0.3, respectively.

A series of hydrogen permeation tests was conducted in a small flat-membrane reactor using 10 μm thick $Pd_{60}Cu_{40}$ membranes (produced from thinning of 25 μm- thick foils). Small inhibitory effects of CO, H_2O, and CO_2 on hydrogen permeation through the Pd-Cu membrane were found at temperatures above 350 ^{o}C. No carbon deposition took place during many hours of membrane operation. The reaction extent on the blank (catalyst-free) membrane was also negligible. At 450 ^{o}C, in a mixture of 10%CO-23%H_2O-10%CO_2-10%He-47%H_2, a H_2 flux of 0.06 mol/m^2/s was measured through the membrane operating at a pressure difference of 2 atm. From these studies, we concluded that operation of the coupled catalyst/membrane system at 450 ^{o}C would be almost free of inhibitory effects on hydrogen permeation. A larger flat- membrane reactor (38 cm^2) is currently being used with the catalyst coated on aluminum screens, close coupled with the $Pd_{60}Cu_{40}$ membrane. Washcoating of etched and oxidized aluminum screens took place by dipping them in an alcohol suspension of the catalyst, which was kept in micronized form by sonication. Global reaction rate measurements and modeling of this system are currently underway.

List of Publications, Presentations, and Students Supported by the Grant

- Q. Fu, S. Kudriavtseva, H. Saltsburg, M. Flytzani-Stephanopoulos, “High-stability water-gas shift catalysts based on nanocrystalline ceria”, 221st National ACS meeting in San Diego, CA, April 1-5, 2001.
- Q. Fu, X. Qi, H. Saltsburg, and M. Flytzani-Stephanopoulos, "TPR and OSC study of nanocrystalline ceria-based catalysts", Annual AIChE meeting, Reno, NV, November 2001, Paper# 358 P.
- M.Flytzani-Stephanopoulos, “Nanostructured cerium oxide ecocatalysts”, MRS Bulletin, Nov. 2001, 885.
- Q. Fu, S. Fiore, H. Saltsburg, X. Qi, and M. Flytzani-Stephanopoulos, " Nanocrystalline ceria-based catalysts for water-gas shift ", 224th ACS National Meeting, Boston, MA, August 2002.
- M. Flytzani-Stephanopoulos, “Novel high-temperature shift catalysts based on Cu-ceria”, Spring Meeting of the New England Catalysis Society, Boston, MA, June 2002.
- X.Qi and M. Flytzani-Stephanopoulos, “ High-temperature water-gas shift on copper-ceria catalysts”, paper submitted to Applied Catalysis B (in review).

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